

Electronic Supplementary Information

Cobalt-Porphyrin /Dansyl Piperazine Complex Coated Filter Paper for “Turn on” Fluorescence Sensing of Ammonia Gas

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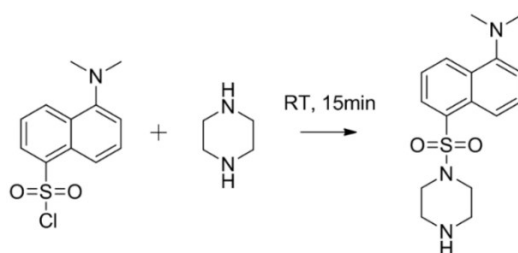
General Methods and Instrumentation

¹H NMR spectra were recorded on a Bruker (Advance III 400) NMR instrument at room temperature with CDCl₃ as solvent. UV-visible and fluorescence spectra were determined on Shimadzu (UV-2450) and Shimadzu (RF-5301PC) spectrometers, respectively. Field emission scanning electron microscope (SEM, FEI-SIRION-100) was used to observe the surface morphology of samples. BET analysis was recorded on the QUANTACHROM AUTOSORB-1-C to measure specific surface area of filter paper. Fluorescence images were taken by Nikon Ti-V inverted fluorescence microscopy from the sensor paper.

Materials and Synthesis

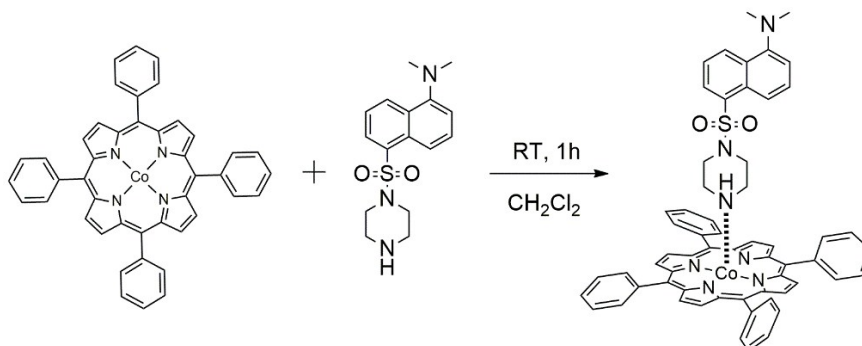
CoTPP: CoTPP was synthesized according to our former work.¹ Co(OAc)₂ (498.2 mg 2 mmol) was added into the solution of tetraphenylporphyrin (307.4 mg, 0.5 mmol) in chloroform (90 ml) and methanol (60 ml). The mixture was refluxed at 60 °C for 3 h. After washing and extraction with water for three times, the organic phase was dried by Na₂SO₄, and CoTPP was recrystallized from acetone after evaporating the solvent.

Dansyl piperazine: Dansyl piperazine (DP) was synthesized according to a standard procedure.² 10 mL solution of dansyl chloride (500 mg, 18.5 mmol) in dichloromethane was slowly added into piperazine (958 mg, 111 mmol) dichloromethane solution (20 mL) in 5 min. The solution was stirred for another 15 min at room temperature. After washing and extraction with water for three times, the organic phase was dried by Na₂SO₄, and then a light green solid was obtained after evaporating the solvent.



Scheme S1. Synthesis of dansyl piperazine.

CoTPP/DP: Cobalt(II)-tetraphenylporphyrin (CoTPP) (13.42 mg, 20 μ mol) was added into a CH₂Cl₂ (10 mL) solution of dansyl piperazine (6.39 mg, 20 μ mol) at room temperature. After continuously stirred for 1 h, a solution of CoTPP/DP was obtained, and the coordination interaction was confirmed by ¹H NMR in Figure S2.



Scheme S2. Synthesis of CoTPP/DP complex.

Coating of CoTPP/DP on filter paper: A piece of filter paper was immersed into deionized water for 2min, followed by immersed into an ethanol solution of tetrabutyl titanate for 5 min. Then, it was soaked in deionized water for 30 min thrice to complete the hydrolytic reaction. The TiO₂ nanoparticle enshased filter paper was obtained after drying at 60 °C for 6 h. This TiO₂ enshased filter paper was immersed into a CH₂Cl₂ solution of CoTPP/DP (1.0 mM) for 5 min, and dried for 1 h at 30 °C.

DP upon addition of CoTPP in dichloromethane. As shown in Figure S3, the addition of CoTPP leads to the fluorescence quenching of DP.

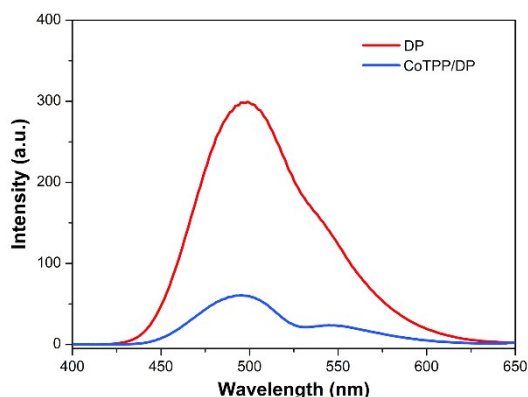


Figure S3. Fluorescence spectra of DP and CoTPP/DP in CH_2Cl_2 solution.

The sensitivity of CoTPP/DP solution upon the addition of NH_3 is illustrated in Figure S4. Addition of 0.5 equivalent of NH_3 to CoTPP/DP solution induces a significant fluorescence emission in 500 nm. There is an increase of about 3.5 folds of emission intensity of fluorescence after the addition of 16 equivalent of NH_3 . No increase of emission intensity was observed after further addition of NH_3 .

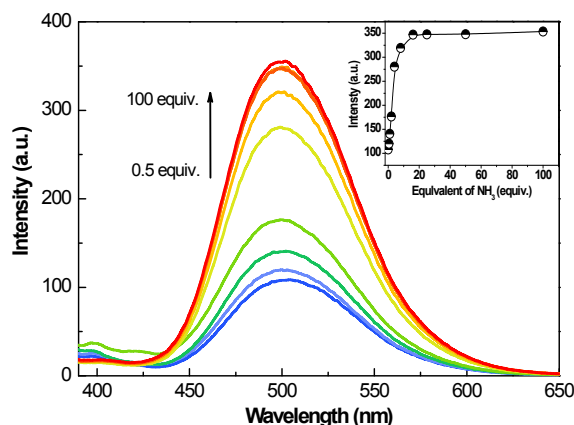


Figure S4. Fluorescence emission changes of CoTPP/DP upon the addition of NH_3 (0-100 equiv.) in CH_2Cl_2 ($\lambda_{\text{ex}}=340$ nm; $\lambda_{\text{em}}=500$ nm; slit width is 5nm).

The binding constant between CoTPP and DP, CoTPP and NH_3 was further studied by absorption spectra and fluorescence spectra. As shown in Figure S5, the absorption of CoTPP decreases in 410 nm, and increases in 429 nm after the addition of NH_3 in CH_2Cl_2 with different concentrations. The binding constant of CoTPP to NH_3 was analyzed by the following *Lineweaver-Burk* equation³:

$$\frac{1}{\Delta A} = \frac{1}{A_0} + \frac{1}{K_a A_0 C} \quad (1)$$

where C is the concentration of added NH_3 , ΔA is the absorbance increase in 429 nm after addition of NH_3 solution, A_0 is the initial absorbance of CoTPP solution (5 μM), K_a is the apparent binding constant. K_a between CoTPP and NH_3 is $(9.719 \pm 0.164) \times 10^4 \text{ M}^{-1}$ calculated by *Lineweaver-Burk* plot in Figure S5 (b).

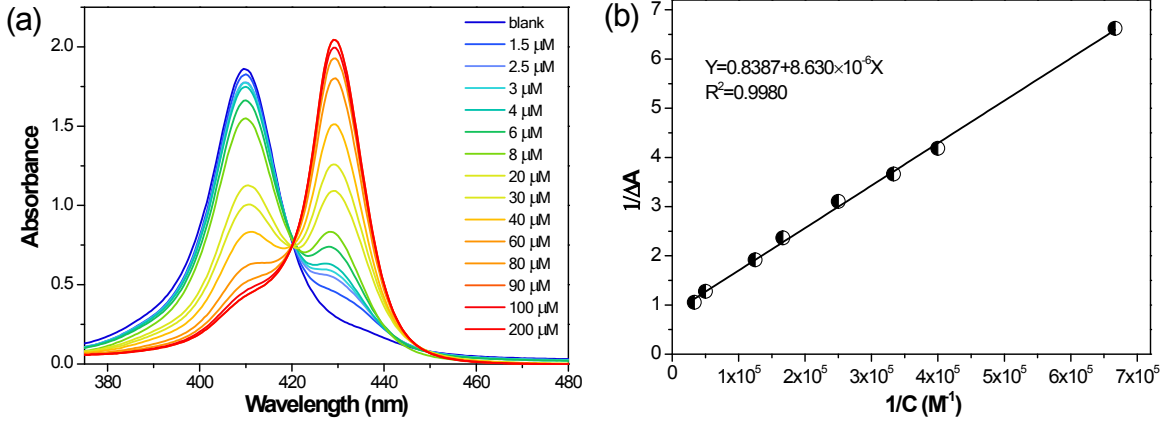


Figure S5. (a) Absorption spectra of CoTPP solution in CH_2Cl_2 upon the addition of NH_3 with different concentrations. (b) *Lineweaver-Burk* plot of NH_3 concentrations versus the absorbance of CoTPP.

The binding constant between CoTPP and DP was also analyzed by fluorescence spectra. Figure S6 shows the fluorescence responses of DP after the addition of CoTPP solution with different concentrations. Increasing the concentration of CoTPP leads to progressive decrease of the fluorescence intensity. The binding constant of CoTPP to DP was analyzed by the following *Lineweaver-Burk* equation:³

$$\frac{1}{\Delta I} = \frac{1}{I_0} + \frac{1}{K_a I_0 C} \quad (2)$$

where C is the concentration of added CoTPP, ΔI is the fluorescence intensity increase (500 nm) after addition of CoTPP solution, I_0 is the initial fluorescence intensity of DP solution (5 μM), K_a is the apparent binding constant. K_a between CoTPP and DP is $(2.154 \pm 0.016) \times 10^3 \text{ M}^{-1}$ calculated by *Lineweaver-Burk* plot in Figure S6 (b).

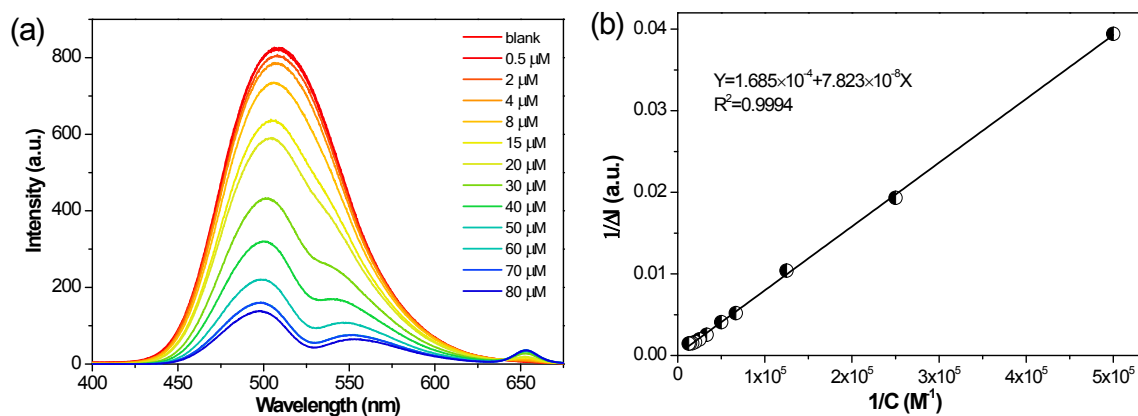


Figure S6. (a) Fluorescence emission changes of DP solution in CH_2Cl_2 upon the addition of CoTPP with different concentrations ($\lambda_{\text{ex}}=340$ nm; $\lambda_{\text{em}}=500$ nm; slit width is 5nm). (b) *Lineweaver-Burk* plot of CoTPP concentrations versus the fluorescence intensity of DP.

As shown in Figure S7, the adsorption hypsochromic shift from 435 nm to 410 nm is attributed to the H-aggregation of CoTPP. After complexing with DP, the adsorption hypsochromic shift in 410 nm of CoTPP is inhibited.

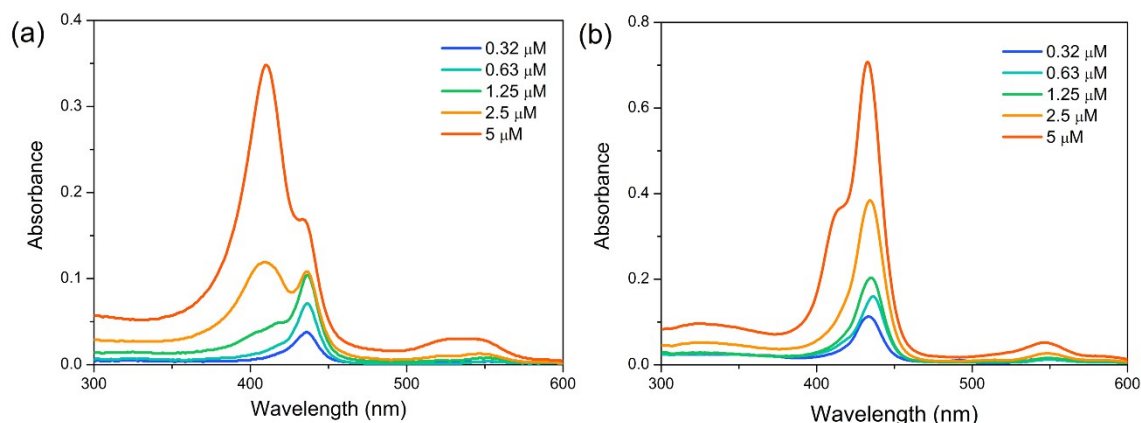


Figure S7 Absorption spectra of (a) CoTPP and (b) CoTPP/DP with different concentrations in CH_2Cl_2 solution.

SEM images of FPs show a complex of microfiber and nanofiber (Figure S8), these composite structure results in high special surface area. After dipping with CoTPP solution, crystal grain was observed on the surface of FP, which was generated by CoTPP aggregation. While coordinate with DP, uniform CoTPP/DP coating was observed instead of the surface coated crystal.

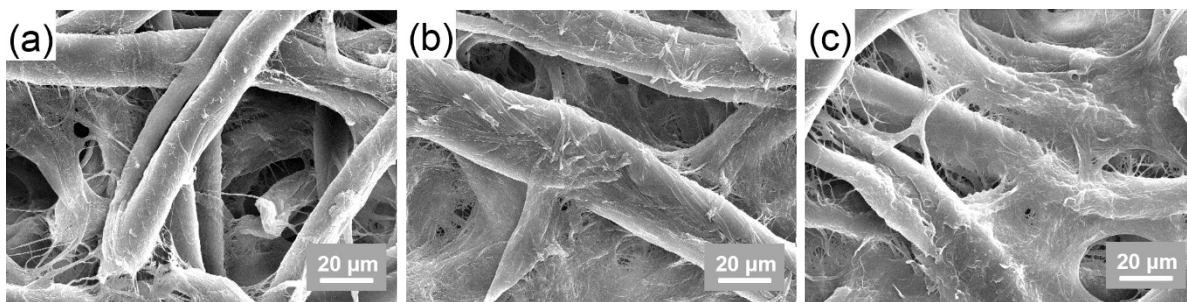


Figure S8. SEM images of FPs: (a) nascent (b) coated with CoTPP (1 mM) (c) coated with CoTPP/DP complex (1 mM).

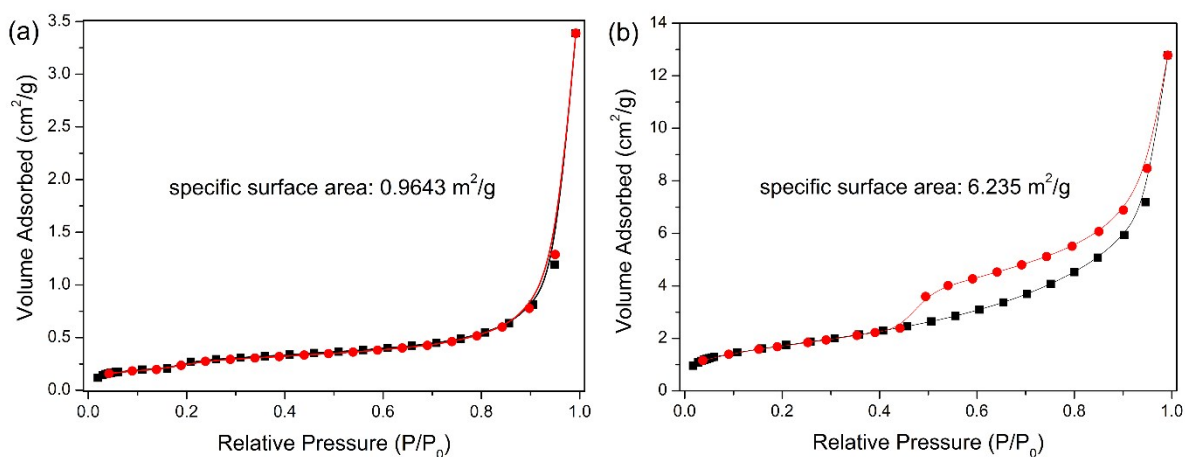


Figure S9. Nitrogen adsorption-desorption isothermal curves of (a) FP and (b) TiO₂ enclashed filter paper

Fluorescence sensing of CoTPP/DP solution and CoTPP/DP coated filter paper to ammonia

The fluorescence response of CoTPP/DP solution to ammonia was studied on Shimadzu (RF-5301PC) spectrometer. Titration experiments were conducted by adding ammonia solution (dissolved in methanol) with different concentrations (0-100 equiv.) into the CoTPP/DP solution (5×10^{-6} M) in dichloromethane. The changes of fluorescence emission were measured after the addition of ammonia solution. Excitation was at 340 nm. Each titration was repeated three times.

The fluorescence response was also measured for CoTPP/DP coated filter papers to ammonia gas. The sensing papers (*ca.* 2 cm × 1 cm) were placed into a sealed testing chamber (500 mL). Then a certain volume of ammonia gas was injected into it through an airtight syringe (Figure S10). The ammonia concentration was controlled by the injection volume. The sample was taken out after 1 min, and then the fluorescence spectra were

measured immediately at excitation wavelength of 340 nm. Each fluorescence sensing process was preformed three times.

Time-course fluorescent response experiments were conducted in a home-made apparatus which was shown in Figure S13(a). The sensing paper was placed into a quartz cuvette testing chamber which was sealed by paraffin wax. Ammonia gas with certain concentration was continuously injected into the quartz cuvette through the tetrafluoroethylene pipe by airtight syringe. At the same time, the fluorescence spectra were measured in time-course mode.



Figure S10. Procedure of injecting the gaseous ammonia into the three-necked flask.

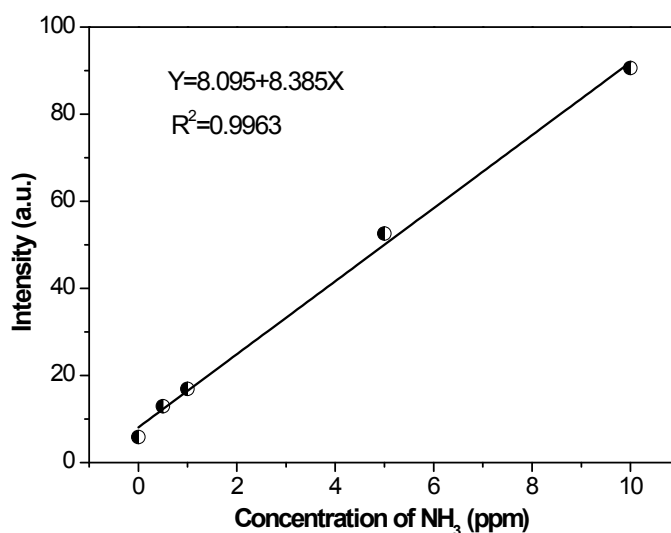


Figure S11. Fluorescence calibration curve of the FPs sensor after exposing to ammonia gas with different concentrations, $\lambda_{em}=511$ nm.

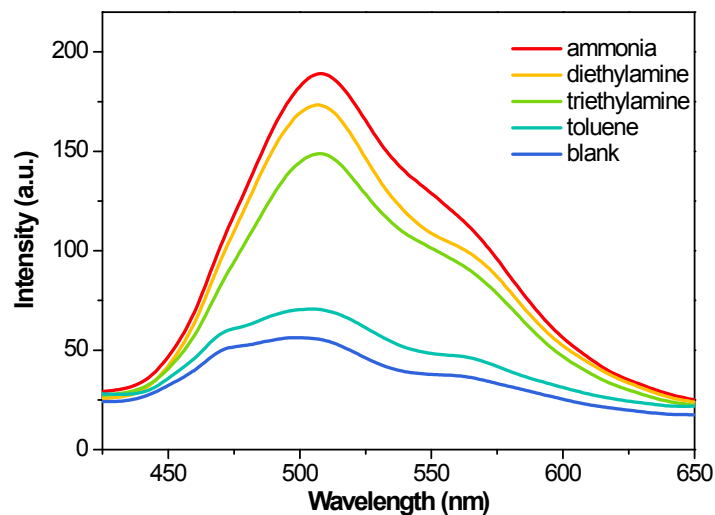


Figure S12. Fluorescence emission changes of FPs sensors upon the addition of different organic amine vapors (100 ppm).

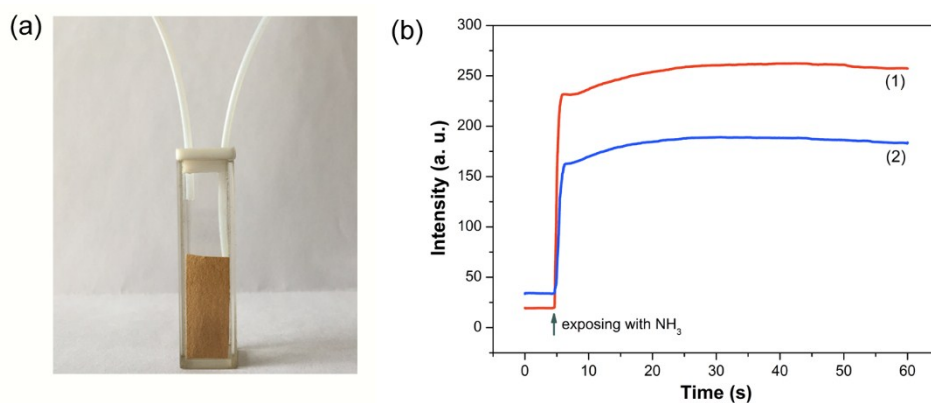


Figure S13. (a) Image of the home-made apparatus for time-course fluorescent response experiment (b) Time-course fluorescent response of (1) CoTPP/DP coated on FPs and (2) CoTPP/DP coated on TiO₂ NPs enshased FPs to NH₃ gas. $\lambda_{em}=511$ nm.

References

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2. S. R. Stauffer and J. F. Hartwig, *J. Am. Chem. Soc.*, 2003, **125**, 6977-6985.
3. Y. Zhang, S. Z. Luo, Y. J. Tang, L. Yu, K. Y. Hou, J. P. Cheng, X. Q. Zeng, P. G. Wang, *Anal. Chem.*, 2006, **78**, 2001-2008.